Improvement of Indoor Air Quality by MDF panels containing walnut shells

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Abstract

High levels of Volatile Organic Compounds (VOCs) and extremes of Relative Humidity (RH) commonly reduce indoor air quality with associated negative effects on human health and wellbeing. Interior materials are known to be one of the main contributors to poor indoor air quality. Notwithstanding, they can also act as a sink for airborne pollutants and excess moisture through adsorption. In this paper, we evaluate the ability of Medium Density Fibreboard (MDF) modified with walnut shell to regulate RH, toluene, limonene, dodecane and formaldehyde. The physicochemical properties, including molecular size/shape, vapour pressure, polarity and boiling point of VOCs allowed them to represent a range of pollutants. Adsorption and desorption behaviour of MDF containing up to 15 % walnut shell was evaluated in two-litre environmental chambers under dynamic conditions at 23 °C and 50 % RH. The porous microstructure of the MDF and walnut shell and their chemical composition were analysed using SEM, XRD and FTIR. Compared to a control panel, walnut shell additions showed an improved ability to remove VOCs and formaldehyde from the indoor air and buffer humidity.

Of particular significance was the irreversible sink effect of formaldehyde and dodecane. This was attributed to the porous surface of walnut shell increasing the specific surface area of the panel and thus its adsorption capacity. The improved capacity of buffer humidity also increased the ability to adsorb water soluble VOCs such as formaldehyde. This research provides for the first time significant evidence that walnut shell modified MDF can improve indoor air quality.

Keywords

Volatile organic compounds, Adsorption/desorption, Medium density fibre board, Walnut shell, Moisture buffering, Occupant health and wellbeing.

1. Introduction

During the past three decades, there has been a growing concern regarding poor indoor air quality attributed to changes in modern building design to conserve energy. The combination of air tightness and high levels of insulation to reduce the heat loss of buildings can lead to an accumulation of gas pollutants in the indoor and an increase in Relative Humidity (RH) [1]. The optimum relative humidity levels are between 40 % and 60 %, with levels outside of this optimum range associated with discomfort, health risks and degradation of some building materials [2–4]. The World Health Organization estimates that, globally over four million deaths were caused by household air pollution in 2012 [5]. Gas pollutants, such as Volatile Organic Compounds (VOCs) and formaldehyde, found in an indoor environment can originate from a wide range of sources such as the outdoors, human activities, furniture and building materials [6–9].

The World Health Organization (WHO) classifies VOCs as organic compounds with boiling points from 50 to 260 °C; below 50 °C they are classed as very volatile organic compounds - VVOCs [10]. Other definitions can be found in the literature such as VOCs eluting from a non-

polar GC column between n-hexane and n-hexadecane, ISO 16000-6:2011 [11]. After a large number of studies on the effects of formaldehyde and VOCs on human health, the WHO guidelines recommend the limit for formaldehyde concentration of 100 $\mu g/m^3$, and across Europe guidelines for total volatile organic compound (TVOC) concentration range from 200 to 500 $\mu g/m^3$ within indoor environments [10,12,13].

Medium density fibreboard is a well-known formaldehyde emitting material due to the formaldehyde based resin used to bind the wood fibres [14]. Commodity resins contain urea formaldehyde and melamine formaldehyde in their manufacture [15,16]. In recent years, legislation and standardisation has reduced the amounts of formaldehyde that can be released from panel products and this has led to research been undertaken to develop of low formaldehyde emission adhesives and scavengers that can been added to the panel to capture the formaldehyde that would otherwise be released into the environment [17–20].

Kim et al. investigated the addition of volcanic pozzolan to the urea-formaldehyde resin to reduce the formaldehyde emission [17]. Pozzolans are usually porous materials composed of siliceous (SiO_2) and aluminous (Al_2O_3) materials [21]. The results confirmed the reduced formaldehyde emissions from the MDF panels with increase of the pozzolan content. The capture of formaldehyde was attributed to the rough and irregular surface, with porous structure, of the pozzolanic materials. Tannin was also added as a formaldehyde scavenger in MDF panels [19]. By adding 1.4 % of tannin solution, the free formaldehyde decreased by 45 %. However, the mechanical properties, such as Modulus of Rupture (MOR) and Internal Bond strength (IB), also decreased with the presence of the tannin. The lower MOR and IB was attributed to the modified fibre structure due to the presence of tannin.

Recently, work has been undertaken to ‘tune’ the properties of the wood fibres by altering the refiner parameters. By changing the refiner pressures Ormondroyd et al. have shown that the

porosity, water sorption and surface energy characteristics can be altered and this can lead to less resin required for panel manufacture and therefore less emissions [22]. In further work assessed the effects of changing the refiner pressure on the ability of the fibre to bond with formaldehyde, it was shown that an optimised refiner pressure can lead to an increase in the absorption of formaldehyde by the fibres [23].

In Iran, walnut and almond shells are considered as agricultural by-products with no significant industrial usage and as a result they are often incinerated or dumped. Pirayesh et al. studied the formaldehyde emission effect of walnut and almond shell addition to particleboards [20]. When 10, 20, 30 and 100 % of shell was added, results showed that the presence of the shells decreased the formaldehyde emission by 42.8 %. The authors attributed the reduction of the formaldehyde emission to the high amounts of extractives in the shells, and therefore the presence of large number of polar hydroxyl and phenolic groups. Wood panels could be produced with up to 20 % of walnut shell particles without falling below the minimum EN standard requirements of mechanical properties for general purpose use [24].

A material can behave as a sink of air pollutants by adsorbing the vapour and then re-emitting it later, the so-called sink effect [25,26]. Building materials that have a good sink effect could improve the indoor air quality by capturing the gaseous pollutants from the indoor air. In the literature, authors often study the adsorption/desorption behaviour (sink effect) of a certain material with regard to a specific VOC or mixture of several VOCs. The physico-chemical interactions of the VOCs with the surface are then considered in relation to properties such as molecular size, boiling point and polarity [27–29]. Also, the experimental conditions such as relative humidity [28,30–32], temperature [28] and air velocity [28,33] are explored. Although, a common observation in these studies is that the lack of data on materials characteristics such

as porosity and other physicochemical properties limit the detailed analysis of the sorption behaviour.

In this study, for a better understanding of VOC and formaldehyde adsorption/desorption behaviour of MDF panels modified with walnut shell, chemical composition of the materials and their microstructure were analysed and correlated with the adsorption/desorption characteristics of several VOCs and formaldehyde. In addition, for a complete assessment of environmental performance, the moisture buffering was also characterised.

2. Materials and Methods

2.1. Materials manufacturing

MDF panels were made to a density of 760 kg/m^3, with area dimensions of 0.4 x 0.4 m^2 and a thickness of 12 mm. The resin loading was 14 % of urea formaldehyde (UF). A commercial mix of spruce, pine and fir chips was refined at 8 bar at the BioComposites Centre, Technology Transfer Centre following the protocols described in [34]. The fibre, scavenger and resin were individually weighed and combined in a drum blender. The resinated fibre was weighed out again and formed into a mat which was subsequently pre-pressed by hand before finally being pressed between two heated platens at 200 °C for 5 minutes following the BioComposites Centre's standard press profile (controlled by the Pressman control program). All samples were transported and stored in sealed bags prior to the characterisation and IAQ assessment. The scavenger loading for the panels was 5, 10 and 15 % of fibre weight, Table 1.

Table 1. % of walnut addition to MDF fibre.

%	Walnut weight (kg)	MDF fibre (kg)
0	0	1.61
5	0.07	1.27
10	0.13	1.20
15	0.20	1.14

2.2. Experimental Methods

2.2.1 Material physical and chemical characterisation

The porous microstructures of the specimen panels were analysed by Scanning Electron Microscopy (SEM) with an acceleration potential of 10kV. Squared sections of each material (10 mm x 10 mm) were cut and fixed to an aluminium sample holder with carbon tape. Prior to the analysis, all samples were sputter-coated with a gold-palladium alloy to increase the electrical conductivity and reduce surface charging. This technique allowed the wood fibre and walnut shell particle size and shape to be determined. It was also possible to observe the dispersion of the walnut shell in the MDF 2-dimensional matrix. High magnifications, above x2000, were used to analyse the walnut shell surface.

To assess the chemical composition of the MDF panels a *Perkin-Elmer Frontier* FTIR spectrometer equipped with a *MIRacle™ Single Reflection ATR* (attenuated total reflectance) with diamond crystal from PIKE technologies was used. The IR spectroscopy was carried out over a wavelength range from 600 to 4000 cm^{-1}, with 2 cm^{-1} of resolution, 25 scans of accumulation and 0.5 cm/s of scan speed. Three spectra were recorded in different zones to validate the data. X-ray diffraction was conducted using a *Bruker-AXS D8* powder X-ray diffractometer operated at 40 kV, 40 mA with a Cu-Kα X-ray source and λ = 1.5405 Å. The sweeping angles (2θ) used were between 5 and 80º with a step size of 0.016 º at ambient

temperature. NIST chemistry Webbook for organic based materials was used as a library for peak identification for both FTIR and XRD results [35].

2.2.2. Moisture buffering

The adsorption and desorption of moisture by the panels due to humidity variation was conducted using ISO 24353:2008 [36]. The humidity was varied every 12 hours; with a step change between 75% and 50% relative humidity; representing the mid-level humidity cyclic test of the standard. All specimens were pre-conditioned at a relative humidity of 63 % and a temperature of 23 °C before cyclic climatic variations were started. Four cycles of 24 hours at the high and low relative humidity at 23°C conditions were run whilst the mass of the specimen was logged.

To ensure vapour exchange only occurred through a single face of the material, the specimens were sealed on the sides and back with aluminium tape. Specimens were cut to 100 mm x 100 mm, with this area exposed to the changing relative humidity environment. The specimens were placed on mass balances, logging every 5 minutes, inside an environmental chamber programmed to subject the specimens to the humidity cycles. To ensure an air speed of 0.1 m/s over the specimens, a screen was placed around the mass balance to minimize the influence of air movement over the surface of the specimens during testing. Fourth cycle moisture adsorption and desorption content values and rates were calculated in accordance with Section 8.3 of ISO 24353:2008. Three samples if each specimen were tested.

2.2.3. Rig for emissions and adsorption and desorption curves of VOCs and formaldehyde

To evaluate the environmental performance of the MDF panels incorporating walnut shell in terms of improving the indoor air quality, adsorption/desorption testing was carried out by exposing the samples to a mixture of formaldehyde, toluene, limonene and dodecane in air. This testing allowed investigation of the capacity of the materials to remove VOCs from the

air when polluted (adsorption) and the release of the adsorbed species when the material was exposed to clean air (desorption). The adsorption and desorption investigations were performed in 2-litre environmental chambers in accordance with BS ISO 16000-24:2009 [37] at Building Research Establishment, Watford, UK. Figure 1 shows a schematic diagram of the rig used to supply air containing VOCs to the 2-litre chamber. The main components of the rig include a pure air generator, chambers containing VOCs and formaldehyde sources, and the 2-litre environmental chambers in which the testing materials are placed. The rig has the capacity to test several materials simultaneously in individual chambers and to run one reference chamber (containing no material) for comparison. Valves placed before the chambers allow the flow of either pure air or dopant air (a mixture of toluene, limonene, dodecane and formaldehyde in air) into the chambers. The maximum concentration generated by the VOC sources was 1800 $\mu g/m^3$ of toluene, 2000 $\mu g/m^3$ of limonene, 2700 $\mu g/m^3$ of dodecane and 590 $\mu g/m^3$ of formaldehyde. The purity of the clean air was analysed and no VOCs or formaldehyde were detected.

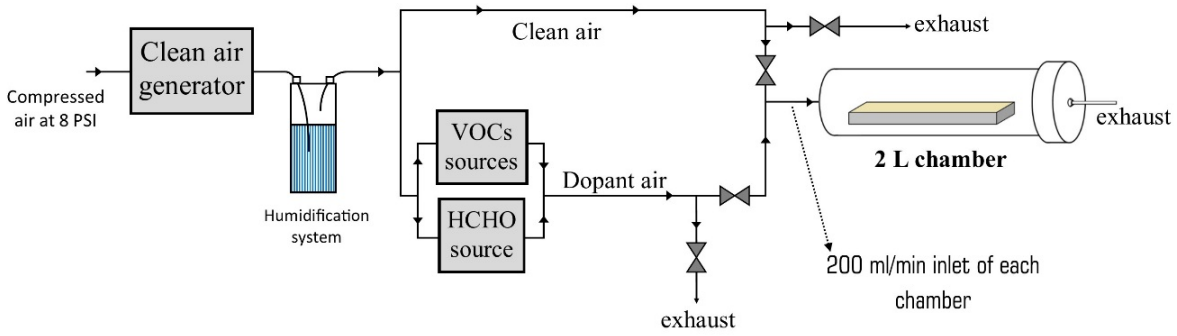

Figure 1. Experimental rig for measuring the adsorption and desorption of VOCs and formaldehyde by the wood panels with walnut shell.

The experiments were carried out under controlled temperature and relative humidity, 23 °C ± 2 °C and 50 % ± 5 %. Mass flow controllers were placed after the pure air generator to adjust

the flow rate of VOCs and formaldehyde sources and the pure air flowing directly to the 2-litre environmental chambers. The inlet flow rate of gas entering the 2-litre chambers was maintained at 200 ml/min. All tubes, valves and joints used in the rig assembly were made of emission-free and non-adsorbing materials. Flow-rates were adjusted with a calibrated Ametek Prime Air flow-meter.

MDF panels were cut into samples with nominal dimensions of 200 mm × 60 mm × 15 mm and sealed with aluminium tape on the sides and back, so that emissions and adsorption/desorption phenomena could occur only from the exposed surface area. Prior to the adsorption/desorption experiment, the testing materials were conditioned inside the environmental chambers for more than 28 days under a flow of pure air. During this period, VOCs and formaldehyde emissions were analysed after 3 and 28 days of conditioning, following the standard BS ISO 16000-9:2006 [38] for VOCs and BS ISO 16000-3:2011 for formaldehyde [39]. After the emissions test and before starting the adsorption/desorption experiment, samples of VOCs and formaldehyde were taken and considered as 0 hour (background) to analyse if the MDF panels were still emitting formaldehyde or VOCs that could affect the adsorption/desorption studies.

During the adsorption/desorption experiment, samples of VOCs and formaldehyde were taken in the outlet of the chambers after 1, 2, 4, 24, 48, 144, 218 and 285 hours of elapsed time during the adsorption phase (dopant air flowing in to the chambers) and 1, 2, 5, 24 and 48 hours in the desorption phase (pure air flowing in to the chambers).

The sampling and analytical procedures for VOCs and formaldehyde were made in accordance with the standards BS ISO 16000-6:2011 [11] and BS EN ISO 16000-3:2011 [39], respectively. Air sampling of VOCs was undertaken in the exhaust of the chambers by using Tenax TA tubes with a flow rate of 150 ml/min for 10 min. The qualitative and quantitative analysis of VOCs

was carried out in an ATD-GC/MS (*Perkin-Elmer*) fitted with a FID detector. Formaldehyde sampling was carried out by using Sep-Pak 2,4-DNPH cartridges at the same flow rate and duration of VOC sampling. After solvent desorption from the 2,4-DNPH cartridges using acetonitrile, the formaldehyde solutions were analysed by HPLC (*Gilson*) equipped with a UV detector. The quality of the VOCs analysis was ensured by analysing an unused Tenax tube and Tenax tubes sampled by spiking stock solutions with known quantities of *n*-hexane, toluene, limonene and *n*-hexadecane to cover the range C_6-C_{16}, named the VOC quality control samples (QCVOCs). The analysed concentration from the QCVOCs had to be within the range of 99 % of the true value calculated by multiplying the standard deviation by a factor of 2. The quality control of formaldehyde was measured by analysing at least two stock solutions with different concentrations of formaldehyde which had the measured concentration with a difference between the known concentration and the measured concentration less than 15 %. Samples of VOCs or formaldehyde were analysed only if the QC samples were within the required range of measured concentration.

All methodologies and instruments used for the IAQ assessment are accredited by UKAS (United Kingdom Accreditation Service). The expanded uncertainty of the VOCs and formaldehyde sampling and analysis was calculated following the standard ISO GUM – JCGM 100:2008 [40]. Because these tests were performed once, the overall expanded uncertainty, with a level of confidence of 99 % (coverage factor of 3), for VOCs was 9.2 % and 8.8 % for formaldehyde. The calculations of the expanded uncertainty included inputs from calibrated flow meters, timing of sampling period, drift of the sampling pump during sampling, laboratory bias, drift of the detector (GC-FID for VOCs and HPLC for formaldehyde).

From previous studies, it is known that the adsorption/desorption behaviour of VOCs is different when present in a mix of several VOCs or alone [41,42]. Because of that, only four

organic compounds were selected to represent a range of molar masses and physicochemical characteristics of VOCs typically found within indoor environments. Toluene was selected as a surrogate of benzene. Limonene is a terpene-type compound and can be emitted by wood-based materials, cleaning products, air-fresheners etc. Limonene has a lower toxicity compared to the other VOCs, although, when in presence of ozone it can react and produces formaldehyde molecules [43]. Dodecane is an alkane with long linear chain with twelve carbon atoms and it is a fuel and oil constituent. Formaldehyde is considered a very-VOC (VVOC) due to its very low boiling point and is of particular importance as it is often found within indoor environments and classified as carcinogenic to humans (Group 1) according to IARC (international agency for research on cancer). In Table 2 the main physicochemical properties of formaldehyde, toluene, limonene and dodecane are presented (ChemSpider database of the Royal Society of Chemistry).

Table 2. Physicochemical properties of formaldehyde and selected VOCs.

	Formaldehyde	**Toluene**	**Limonene**	**Dodecane**
Formula	CH_2O	C_7H_8	$C_{10}H_{16}$	$C_{12}H_{26}$
Chemical conformation	Simple	Aromatic	Cyclic	Straight chain
Polarity	Polar	Non-polar	Non-polar	Non-polar
Molar mass (g/mol)	30	92	136	170
Vapour pressure (mm Hg at 25 °C)	3890	28.4	1.45	0.135
Water solubility (mg/l at 25 °C)	400000	526	13.8	0.0037
Boiling point (°C)	-19	111	176	216

3. Results and discussion

3.1. Microstructure

Scanning electron microscope images of the MDF panels with walnut shell are presented in Figures 2 a) to d). MDF panels were manufactured to achieve a density as close to 760 kg/m^3 as possible. It became apparent however that packaging of the wood fibres in the MDF panels with higher contents of walnut shell led to a more compact structure than expected. This resulted in the voids between each single wood fibre in the MDF matrix being smaller for the panels with higher contents of walnut shell which led to a higher surface area, Figure 2 d). Materials with higher surface area will have a greater surface available to adsorb molecules of VOCs and water.

Figure 3 shows the walnut shell particles embedded in the MDF matrix.

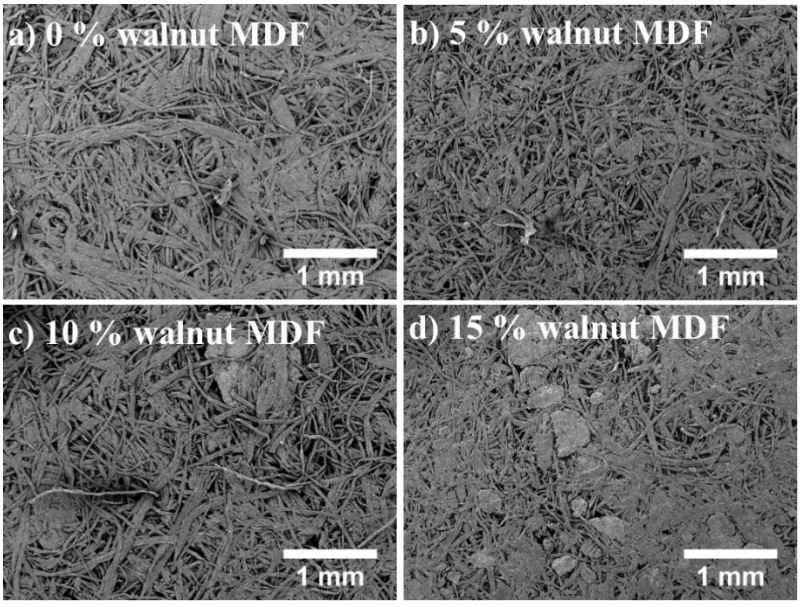

Figure 2. Scanning electron microscopy images of a), b), c) and d) MDF panels with walnut shell at x30 of magnification.

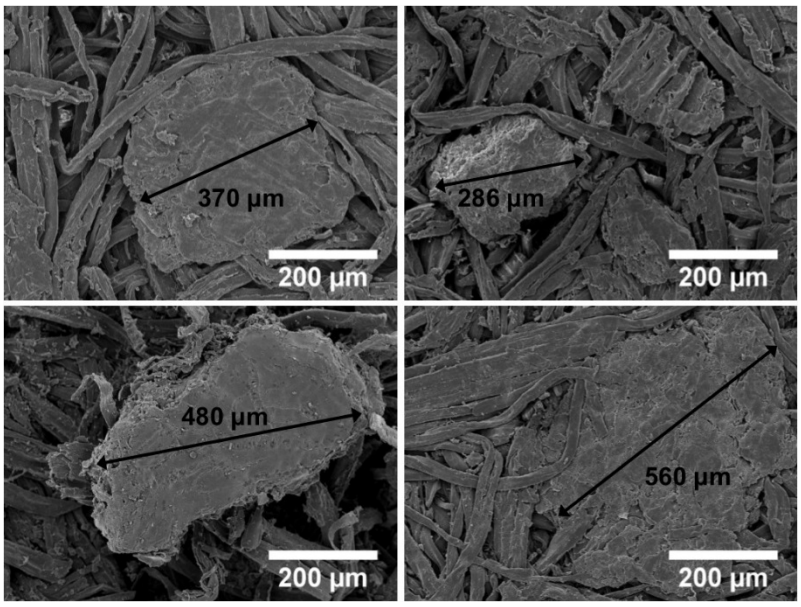

Figure 3. A number of representative scanning electron microscopy images of walnut shell particles of varying size.

Macroscopically, walnut shell does not show porosity as seen in Figure 3 although, at higher magnifications a highly porous structure can be observed, Figure 4 a) and b). The wood fibre surface is shown in Figure 4 c) and d). The average size of the pits in the wood fibre is 1.42 µm.

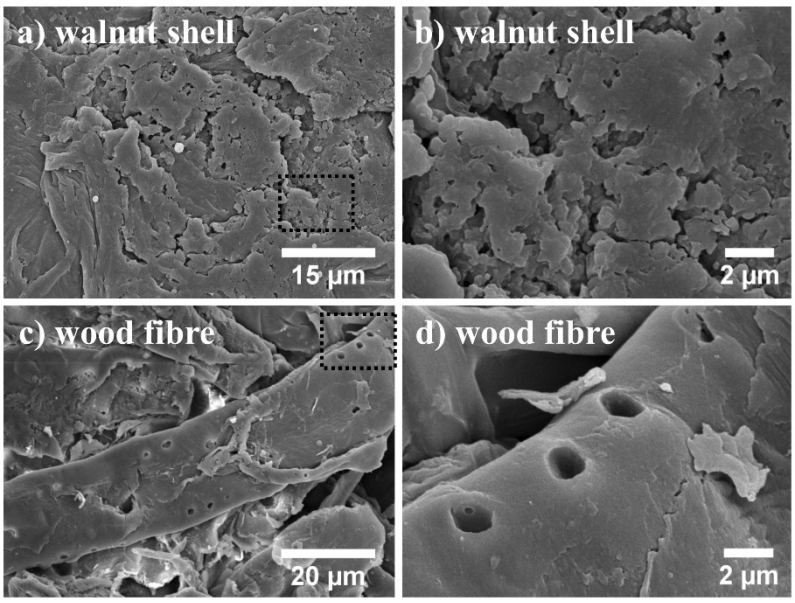

Figure 4. Scanning electron microscopy images of a) and b) the walnut surface, c) and d) MDF wood fibre surface. Images b) and d) are higher magnifications of the dashed areas indicated in a) and b), respectively.

Walnut shell presents an irregular porous surface with pore sizes ranging from 25 nm to 1224 nm. The pore size of the walnut shell was measured using ImageJ version 1.48 image analysis software. An average pore size of 330 nm was obtained from a sample of two hundred measurements. As the pore size distribution is wide the average is not representative and thus it is plotted as a size distribution, Figure 5. In a sample of 200 pore size measurements, 20 % of the pores exhibited sizes between 25 and 74 nm. Overall, 65 % of all measured pores showed sizes below 374 nm.

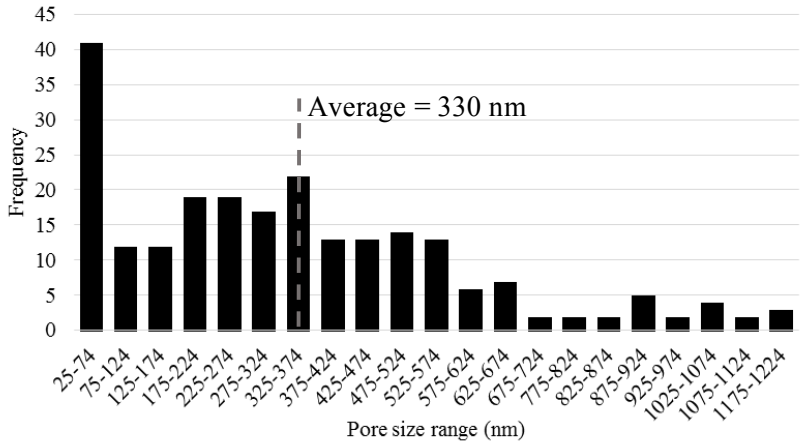

Figure 5. Pore size distribution of the walnut shell.

In Figure 6, an FTIR spectrum and X-ray diffractogram of the reference MDF panel (no added walnut) are shown. Characteristic bands for cellulose, hemicellulose and lignin were identified in the FTIR spectrum. Stretching vibrations of hydroxyl groups present in the cellulose molecule such as –CH-OH and –CH_2-OH are shown in the 3400 to 3300 cm^{-1} wavelength range. Stretches of –CH and –CH_2 groups occur at 2918 and 2852 cm^{-1} range. The surface –

OH bending vibrations are verified around 1645 cm^{-1}. The range from 1500 to 1200 cm^{-1} relates the primary and secondary hydroxyl bending and the C-O stretching vibration is observed at 1261-1028 cm^{-1}. In the X-ray diffractogram, Figure 6 b), two peaks from the semi-crystalline cellulose are shown at 2θ values of 16 and 23°.

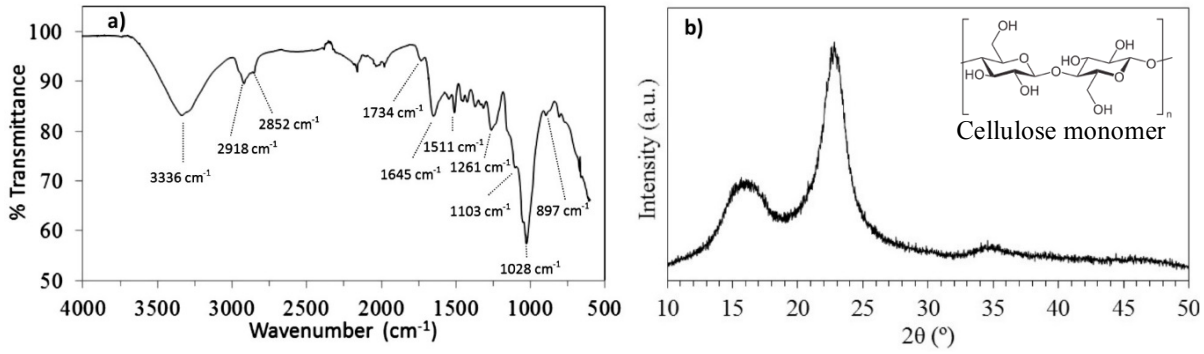

Figure 6. a) FTIR spectrum and b) X-ray diffractogram of MDF.

3.2. Moisture buffering

The moisture adsorption and desorption characteristics of the MDF control specimen (0 % walnut) and specimens with 5, 10 and 15 % walnut shell are presented in Figure 7. Three specimens of each variation type were tested and the error bars represent the 95 % confidence interval. Although an alternative method was used, the results can be compared against classifications for moisture buffering of materials proposed by Rode et al. [44]. The MDF panel without any modification would be classified as *good*. Panels containing 10 % and 15 % walnut shell exhibited improvements of 34 % and 44 % respectively, leading to a moisture buffering material classification of *excellent*.

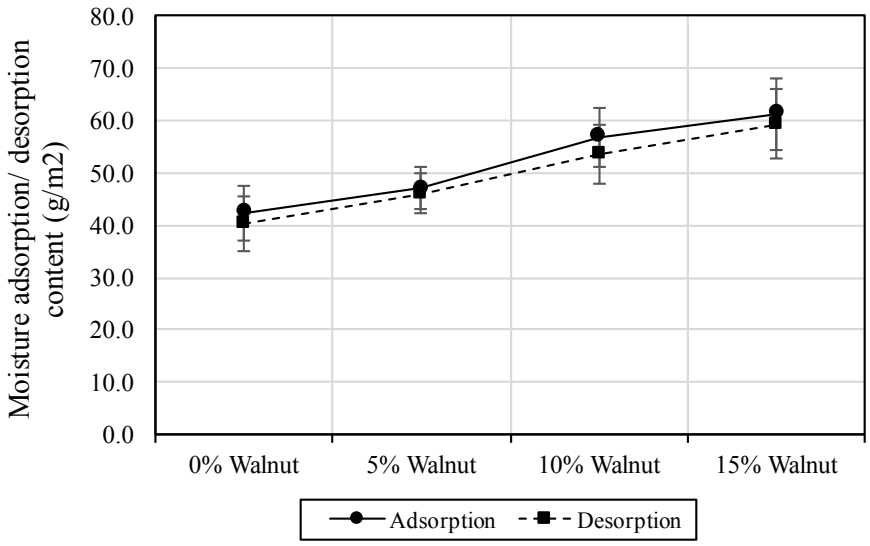

Figure 7. Moisture adsorbed by MDF panels with walnut shell.

3.3. VOCs and formaldehyde emissions

Emissions tests were carried out by passing only pure air through the chambers. Air in the exhaust of the chambers was sampled after 3 and 28 days as per BS EN ISO 16000-9:2006. The concentration of formaldehyde and total-VOCs in the chamber was then calculated as the area specific emission rate ($\mu g/m^2$ h), Figure 8. The main VOCs identified during emissions testing were acetic acid and 2-ethylhexane-1-ol. Acetic acid emitted by the MDF panels can be associated with the degradation of the hemi-cellulose by the elimination of acetyl-groups [45,46]. This could be caused due to the heat-treatment applied to the MDF panels during the manufacturing process as described in the experimental section.

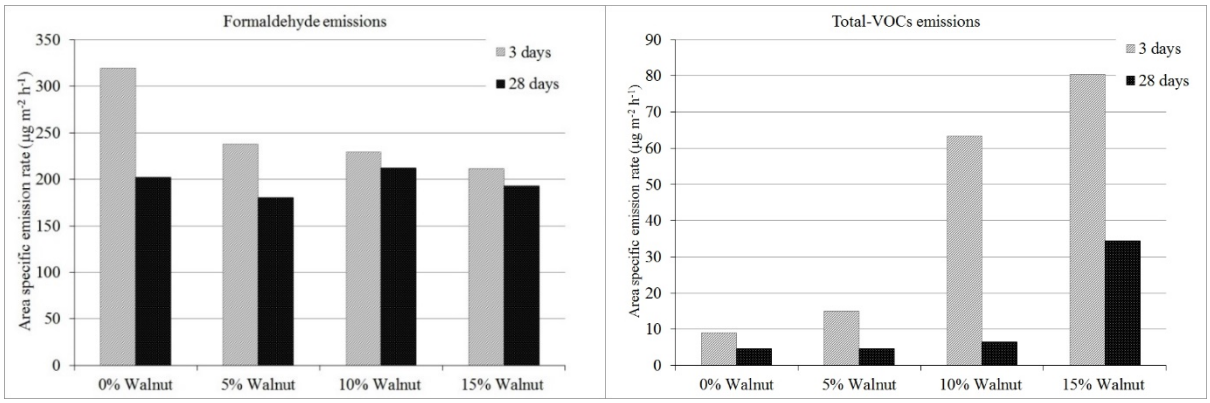

Figure 8. Area specific emission rate of formaldehyde and total-VOCs from the wood panels. Major VOCs emitted: acetic acid and 2-ethylhexane-1-ol.

Formaldehyde emission rate was lowest for the MDF panel with 15 % walnut shell content after 3-days of testing. In comparison, the MDF panel with the highest walnut content emitted 34 % less formaldehyde than the MDF without walnut. Pirayesh et al. [20] also observed a decrease in formaldehyde released by the particleboard with higher walnut content using the BS EN 717-3 [47] standard methodology. Similar observations were reported in other studies [19,48]. After 28-days, the MDF panel with 5 % walnut showed the lowest emission rate with 180 µg/m^2 h followed by the MDF with 15 % walnut with 193 µg/m^2 h. Notwithstanding the decreasing emission rate with increasing walnut content at 3-days emission, at 28-day testing, the difference between all samples was reduced, being only 15.1 % difference between the sample with the highest and lowest emission rates, 180 to 212 µg/m^2 h. Kim et al. [49] reported slightly higher 3-day formaldehyde emissions from MDF panels, 400 µg/m^2 h. Unlike the formaldehyde emissions, TVOC emissions increased with the addition of walnut from 9 to 80 µg/m^2 h with 15 % of walnut added after 3-days of testing. After 28 days, MDF with 0 %, 5 % and 10 % showed very low emissions of 5, 5 and 6 µg/m^2 h, respectively. The respective concentrations in the chambers were almost within the range of the lowest limit of quantification (LOQ) of the GC/MS system, 3 µg/m^3. Further investigation is required to fully

understand why the TVOC emission increases with the addition of walnut, despite being very low. Significantly higher 3-day TVOC emissions were reported by Kim et al. [49] and Son et al. [50] of 300 μg/m^2 h and 460 μg/m^2 h respectively. In an adsorption process two types of interactions can occur between the solid and fluid phase: physisorption and chemisorption [51]. The chemical nature of the material and its physical characteristics (*e.g.* open porosity, pore size distribution *etc.*) will determine if the interaction between the material surface and the organic pollutants is physical, chemical or even a combination of both, [6,52]. Da Silva et al. suggested that interactions between building materials and organic pollutants are a combination of physical and chemical processes [6,52]. Materials such as cellulose from the wood fibres which have high surface area and chemical components with negative/positive charges or hydroxyl groups typically exhibit a combination of physisorption and chemisorption when exposed to organic pollutants. In the case of MDF panels, the reduction of formaldehyde emissions with the increase in walnut shell content can be attributed to the porous microstructure of shell surface leading to a higher specific surface area and hydroxyl groups present in the chemical components of the material as discussed previously.

3.4. VOCs and formaldehyde absorption/desorption

The adsorption and desorption behaviour of MDF panels with walnut shell are shown in Figure 9. Adsorption/desorption curves represent the concentration of formaldehyde and VOCs in the chambers of each material plotted over the elapsed time. The difference of concentrations in the reference chamber and a chamber containing a material is the amount of VOC adsorbed on to the material surface. Concentrations of the black line with squares represent the adsorption/desorption phase in the reference chamber. These concentrations are dependent on the emission rate of the VOCs and formaldehyde sources. Toluene and formaldehyde sources

showed a stable emission rate, but the emission rates of limonene and dodecane sources increased over the elapsed time reaching their maximum after 215 hours.

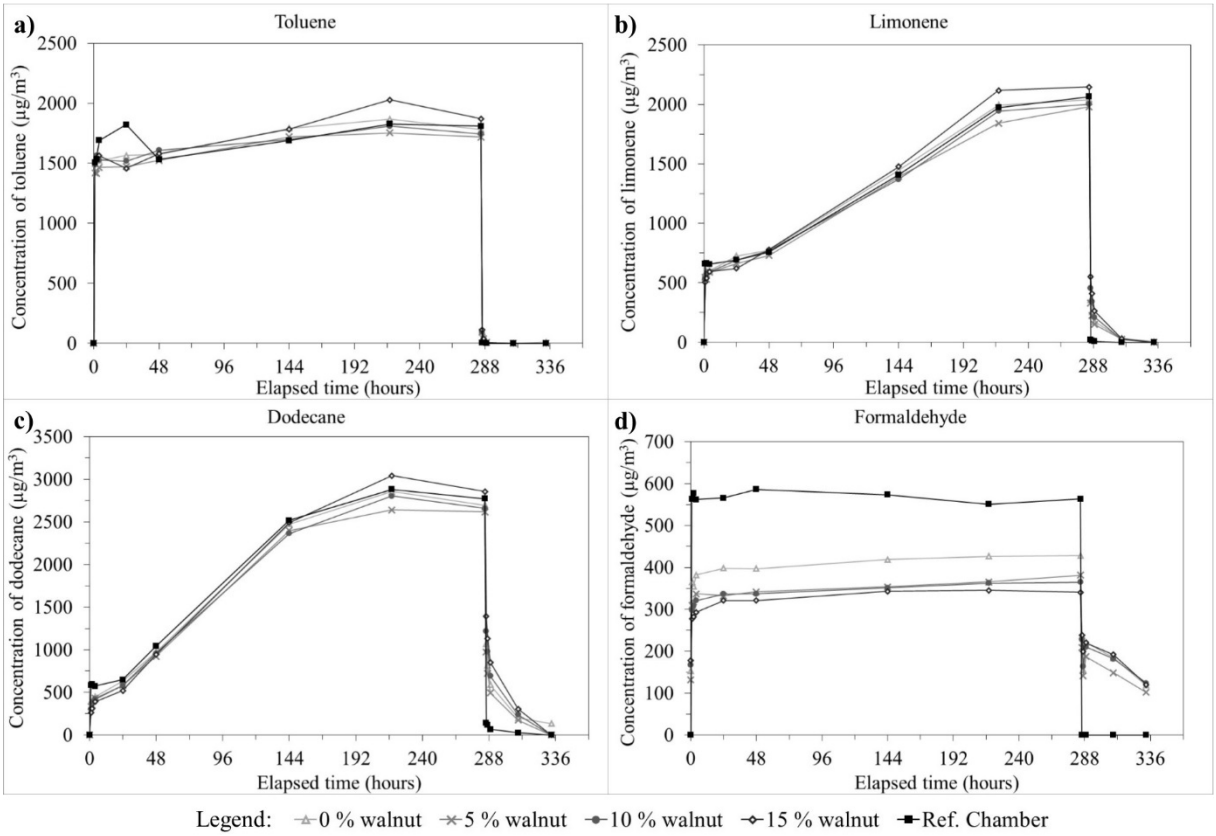

Figure 9. Adsorption/desorption curves of a) toluene, b) limonene, c) dodecane and d) formaldehyde.

Considering the adsorption and desorption behaviour of all samples with respect to the four pollutants, toluene was the least adsorbed volatile compound and formaldehyde was the most. This indicates that less polar molecules have a lower affinity for adsorption compared to those with higher polarity such as formaldehyde. Aromatic and cyclic compounds, including toluene and limonene, were the least adsorbed. Similar observations were made by Da Silva et al. [6], Mansour et al. [53] and Niedermayer et al. [29]. Dodecane was more preferentially adsorbed compared to toluene and limonene because it is a larger linear hydrocarbon chain and so has

more oscillating charges associated with its electron cloud that can interact with electron clouds from the materials [54]. This facilitated the diffusion through pores and capillaries of the walnut shell and wood fibre by physisorption [55]. Also, the lower vapour pressure would facilitate the physisorption of dodecane compared with toluene and limonene. At the end of the adsorption phase, the MDF sample with 15 % of walnut showed higher concentrations of limonene and dodecane in the chamber than the reference chamber. Further research needs to be done to understand this case. During the desorption phase, no toluene was detected in any chamber after five hours from the start of this phase. At 48 hours, dodecane was still being desorbed by the pure MDF and formaldehyde desorbed by all the materials.

The adsorption (up to 24 hours) and desorption (up to the end of the experiment) behaviour of formaldehyde by the MDF panels is shown in detail in Figure 10.

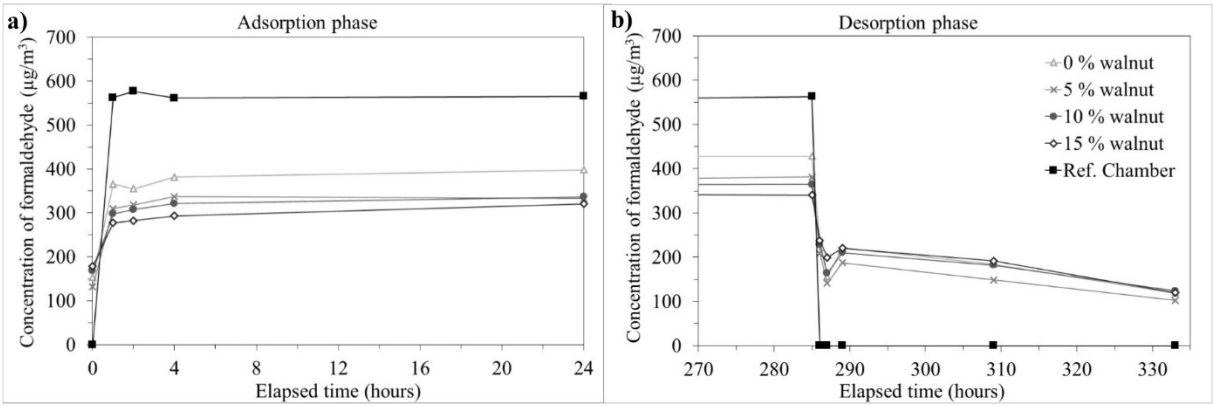

Figure 10. a) Adsorption curve of formaldehyde in detail and b) desorption curves of formaldehyde in detail by the wood panels with walnut.

Figure 10 a) shows the concentration of formaldehyde reached its maximum in the reference chamber after one hour and remained almost constant until the end of the adsorption phase at 285 hours. During the desorption phase, Figure 10 b), the concentration of formaldehyde dropped immediately to 0 µg/m^3 in the reference chamber. Interestingly the MDF containing

15 % walnut exhibited the lowest concentration of formaldehyde during the adsorption phase, figure 9 a), indicating that the MDF with higher content of walnut shell has a strong adsorption efficiency with regard to formaldehyde. In addition to the polarity of the formaldehyde, its high water solubility may also have a great influence on its adsorption by materials. Investigation of the moisture buffering of the MDF panels with walnut shell incorporated showed that materials with the highest walnut shell content possess the greatest ability to adsorb water vapour. In this case, considering that materials surface has a layer of condensed water, formaldehyde molecules would be therefore absorbed onto this layer. In the case of the water molecules being in gaseous phase, both formaldehyde and water molecules would compete for the available adsorption sites since both compounds are polar. Ruiz et al. [56] studied the effect of water vapour on ketone adsorption by soil minerals. The authors observed that for lower VOC concentration at higher relative humidity, the adsorption capacity of the VOC was reduced, suggesting that polar VOC molecules compete with water vapour molecules for the adsorption sites in the soil surface. However, at higher concentrations of VOC, the adsorption capacity was not so much reduced due to the similar intensity of polarity of both compounds. Further research needs to be undertaken in order to better understand the interactions between formaldehyde and the surface of the MDF panels with walnut shell incorporated at different levels of relative humidity.

A small perturbation at the beginning of the desorption phase, at 285 hours, is visible in figure 10 b). For all samples the formaldehyde concentration in the chamber dropped to a minimum at 287 hours before increasing again to a slightly higher value at 290 hours. This behaviour is consistent with two desorption processes taking place on/in the sample surface over these first few hours of desorption. It is beyond the scope of this investigation to confirm the exact nature of these, however it could be hypothesised that a proportion of the formaldehyde is surface adsorbed and can be released quickly into the pure air atmosphere. In addition, there may be

formaldehyde present in the sub-surface pore network of the sample which must negotiate a diffusion path before final release into the chamber atmosphere, which would take more time. This behaviour may be a consequence of the difference in chemical and physical properties of the wood fibre and walnut shell phases present in the test specimens.

The amount of formaldehyde and dodecane adsorbed and desorbed by the MDF panels during the adsorption and desorption phases is shown in Figure 11 a) and b), respectively. The mass of VOC adsorbed or desorbed was calculated as a product between the volumetric air flow through the chambers and the difference between concentrations in the test chamber and reference chamber, integrated over the period 0 to t hour period; being t = 285 hours for the adsorption phase and t = 48 hours for the desorption phase. The amount of formaldehyde adsorbed by the MDF panels increased from 528 µg to 798 µg when 15 % of walnut shell was added. MDF samples with 5 and 10 % of walnut shell showed similar amount of formaldehyde adsorbed, 729 and 745 µg, respectively. The difference between the mass of formaldehyde adsorbed and desorbed is the amount of formaldehyde that is still adhered to the material surface. If the desorption phase was carried out until the concentration in all chambers was 0 µg/m^3, this difference would represent the irreversible adsorption of formaldehyde. Although, as shown in Figure 9, at 333 hours of elapsed time (48 hours since the desorption phase started) all materials were still desorbing formaldehyde. On the other hand, in the case of dodecane Figure 8, all chambers showed a concentration of 0 µg/m^3 (except 0 % walnut MDF showing 134 µg/m^3), which means that MDF panels with 5, 10 and 15 % desorbed all physisorbed dodecane after 48 hours of the desorption phase started. In this case, Figure 11 b) presents the amount of dodecane irreversibly adsorbed by the MDF panels with 5 and 10 % of walnut (good sink effect). Pure MDF desorbed almost the same amount of dodecane that had been adsorbed. In the case of MDF with 15 % of walnut, the amount of dodecane desorbed is higher than the amount adsorbed. This is the result of the concentration of dodecane in the chamber containing

MDF with 15 % walnut being higher than the concentration in the reference chamber. Further research must be carried out to fully understand this case.

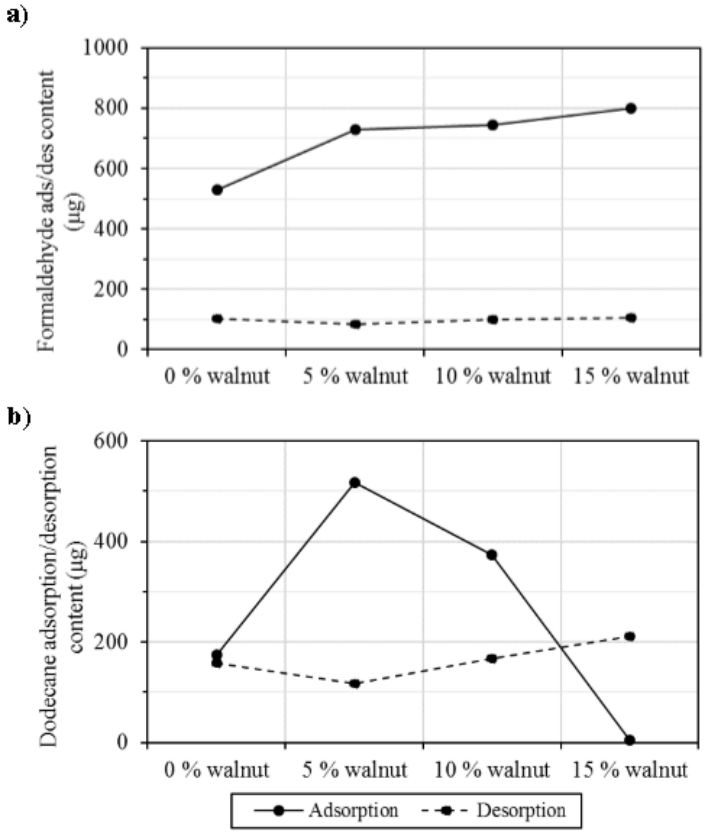

Figure 11. Amount of (a) formaldehyde and (b) dodecane adsorbed after 285 hours and desorbed after 48 hours for MDF panels containing 0, 5, 10 and 15% walnut shell.

4. Summary and conclusions

This study demonstrates the ability of MDF panels containing walnut shell to improve the indoor air quality. This achieved through lower initial emissions, removal of organic pollutants, and improved moisture buffering properties performed under lab-scale conditions. MDF panels with higher walnut shell contents showed a greater ability to adsorb organic pollutants and moisture. Polar compounds, such as formaldehyde and water, and compounds with linear molecular chains, such as dodecane, were adsorbed more readily by all materials when

compared with the cyclic compounds such as toluene and limonene. The removal of formaldehyde from the air was observed not only during the adsorption/desorption tests but also during the emissions testing. As well as the polarity of formaldehyde, its solubility in water can also be the reason for the better ability of the MDF with walnut shell to adsorb this compound, since the same material adsorbed more water during the moisture buffering analysis. Further studies need to be undertaken in order to investigate the effect of the presence of the water vapour on the formaldehyde adsorption and desorption. Despite the present study being focused on the environmental performance of the MDF panels modified with walnut under ambient conditions to simulate the real conditions inside a building (i.e. 23 °C and 50 % RH), an interesting study would be to perform the VOCs and formaldehyde adsorption/desorption experiment at much lower relative humidity, i.e. dry conditions, to avoid the effect of water solubility of VOCs. MDF panels with 5 and 10 % showed irreversible adsorption of dodecane which is an irreversible sink effect. The incorporation of walnut within the MDF panels showed excellent promise for the future of MDF as a building material. This is particularly important as MDF could be identified as a problematic material due to its high formaldehyde emissions and negative impacts on the health and wellbeing of humans exposed. Adoption of walnut shell as an additive in fibre-based building materials will not only improve indoor air quality, but also provide an alternative to landfill or incineration of the shell, with an associated reduction in embodied CO_2. Real-scale testing of these materials should be done in order to understand their behaviour under realistic conditions.

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